Four component regular relativistic Hamiltonians and the perturbational treatment of Dirac's equation

Sadlej, A. J.; Snijders, J. G.; van Lenthe, E.; Baerends, E. J.

Published in:
Journal of Chemical Physics

DOI:
10.1063/1.468703

Four component regular relativistic Hamiltonians and the perturbational treatment of Dirac's equation

A. J. Sadlej, J. G. Snijders, E. van Lenthe, and E. J. Baerends

Citation: The Journal of Chemical Physics **102**, 1758 (1995); doi: 10.1063/1.468703
View online: https://doi.org/10.1063/1.468703
View Table of Contents: http://aip.scitation.org/toc/jcp/102/4
Published by the American Institute of Physics

Four component regular relativistic Hamiltonians and the perturbational treatment of Dirac's equation

A. J. Sadlej,[a] J. G. Snijders, E. van Lenthe, and E. J. Baerends
Department of Theoretical Chemistry, Vrije Universiteit, De Boelelaan 1083, 1081 HV, Amsterdam, The Netherlands

(Received 22 August 1994; accepted 22 September 1994)

By combining the ideas of the direct perturbation theory approach to the solution of the Dirac equation with those underlying the regular expansion as used to obtain the two-component Chang–Pélissier–Durand Hamiltonian, a four-component form of the regular expansion is proposed. This formulation lends itself naturally to systematic improvement by a nonsingular form of perturbation theory. Alternatively it can be viewed as a double perturbation version of direct perturbation theory, where relativistic effects on the Hamiltonian and the metric are considered separately and the Hamiltonian perturbation is summed to infinite order. The scaling procedure that was earlier shown to be exact in the case of a hydrogenic potential and that greatly improved the core orbital energies, is found to follow naturally from the current formulation. The accuracy of the various approximations to the wave functions is assessed with respect to several radial expectation values weighing different regions in the uranium atom as a test case. © *1995 American Institute of Physics.*

I. INTRODUCTION

It is well known that relativistic effects are very important in the study of the chemistry of heavy elements. Although instead of the Schrödinger equation one then has to solve a many electron generalization of the four-component Dirac equation, fully relativistic calculations are not intrinsically more complicated than nonrelativistic ones. They are, however, very time consuming, even at the self-consistent field (SCF) level, due to the need of complex arithmetic and the large dimensions of the resulting secular problem caused by the presence of four components. Moreover one has to ensure that no spurious solutions appear, which can be done by using so-called kinetically balanced basis sets, but then one needs an even larger basis for the small component than for the large component of the Dirac spinor, leading to a substantial increase in computational effort.

Consequently it is still desirable to search for sufficiently accurate approximate relativistic methods that can be applied to larger systems than those that can be treated by the full Dirac theory. We refer to the discussion by Kutzelnigg[1] for a detailed exposition of the various approaches proposed.

In a series of papers[2–7] we have shown earlier that the difficulties with divergent operators encountered in several of these methods, are caused by their implicit or explicit reliance on expansions in $(E-V)/2c^2$. Such an expansion is in fact invalid for particles in an attractive Coulomb potential, for which there will always be a region of space (close to the nucleus) where this expansion parameter is not small. This problem was then avoided by using an alternative expansion parameter $E/(2c^2-V)$, which for valence energies remains small over all space, leading to two-component relativistic Hamiltonians that are, at least in the lowest order, variationally stable and contain similar relativistic corrections as those present in the Pauli Hamiltonian but in a regularized form. In its simplest form the regularized Hamiltonian turns out to be identical to the one derived earlier by Heully *et al.*,[8] Durand,[9] and Chang, Pélissier, and Durand[10] using the theory of effective Hamiltonians. This regularized operator will be referred to as the CPD Hamiltonian.

In this paper we will introduce a four-component form of the CPD method (referred to as CPD-4), which in view of the computational efficiency gained by using two- or even one-component methods,[2,3,7] may seem like a step backward. However, it will be shown that by an analysis of the four-component CPD formalism one can achieve a deeper understanding of the mathematical origin of the two-component method and link it directly to the direct perturbation theory (DPT) formalism proposed by Rutkowski[11] and Kutzelnigg.[1,12,13] This gives a nice example of the efficiency of the partial infinite summation techniques in perturbation theory as a tool for avoiding divergencies, such as have been used in many-body theory for a long time (see, e.g., Ref. 14). After this partial summation has been performed the resulting theory can be cast into a form where the remaining relativistic perturbation affects only the metric, rather than the Hamiltonian. Moreover, the CPD-4 method provides a straightforward derivation of the ''scaled'' CPD method[3,6] that was earlier shown to give very accurate energies and generalizes it to the calculation of other expectation values.

Although the analysis of the CPD method is carried out in this paper in terms of the four-component formalism, this hardly affects the computational aspects of our approach. All numerical calculations involve essentially only the large component solutions, the small components being always generated from them by using regular (nonsingular) energy independent operators. The method easily lends itself to the generation of higher order approximations and we will propose two methods that are correct through first order in the renormalization perturbation and which will be shown to

[a]Permanent address: Theoretical Chemistry, University of Lund, Box 124, S-22100 Lund, Sweden.

 0021-9606/95/102(4)/1758/9/$6.00

give very accurate results even for very deep lying core levels.

In order to test the various schemes proposed in this paper, we have applied them to the calculation of energies and several radial expectation values in the case of the uranium atom and we have analyzed these results in detail to assess which level of approximation is appropriate under which circumstances. It should be pointed out that, since a Foldy–Wouthuysen type transformation is not performed and a four-component formalism is retained, we can make direct comparisons to full Dirac expectation values, without complications that arise from changes in picture.[15,16]

II. THE RENORMALIZATION PERTURBATION THEORY OF THE DIRAC EQUATION

As shown by Rutkowski[11] and Kutzelnigg[1,12,13] additional insight into the Dirac equation and its relation to the nonrelativistic Schrödinger eigenvalue problem can be obtained by writing it in a modified metric (α is the inverse of the speed of light, atomic units are used throughout)

$$H^D\Psi^D \equiv \begin{bmatrix} V & \boldsymbol{\sigma}\cdot\mathbf{p} \\ \boldsymbol{\sigma}\cdot\mathbf{p} & \alpha^2 V-2 \end{bmatrix}\Psi^D = W^D(S^0+\alpha^2 S^2)\Psi^D, \quad (1)$$

where the four-component solution Ψ^D is normalized in the $S^0+\alpha^2 S^2$ metric,[1,13]

$$\langle \Psi^D | S^0+\alpha^2 S^2 | \Psi^D\rangle = \langle \varphi^D|\varphi^D\rangle + \alpha^2\langle \psi^D|\psi^D\rangle = 1 \quad (2)$$

and φ^D and ψ^D denote the large and small two-spinor components of Ψ^D,

$$\Psi^D = \begin{bmatrix} \varphi^D \\ \psi^D \end{bmatrix}, \quad (3)$$

respectively. $H^D = H^D(\alpha)$ in Eq. (1) is the Dirac Hamiltonian adapted to the metric defined by Eq. (2). The metric matrices are given by

$$S^0 = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}, \quad S^2 = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}. \quad (4)$$

In what is referred to as the direct perturbation theory (DPT),[13] all terms in Eq. (1) which involve α are considered as a perturbation to what is known as the Levy–Leblond equation,[13,17,18] which is essentially equivalent to the nonrelativistic Schrödinger equation (for the differences see Ref. 12)

$$\begin{bmatrix} V & \boldsymbol{\sigma}\cdot\mathbf{p} \\ \boldsymbol{\sigma}\cdot\mathbf{p} & -2 \end{bmatrix}\Psi^{\mathrm{LL}} = W^{\mathrm{LL}} S^0 \Psi^{\mathrm{LL}}, \quad (5)$$

where Ψ^{LL} is normalized as

$$\langle \Psi^{\mathrm{LL}} | S^0 | \Psi^{\mathrm{LL}}\rangle = \langle \varphi^{\mathrm{LL}} | \varphi^{\mathrm{LL}}\rangle = 1 \quad (6)$$

and φ^{LL} is the large component of the four-spinor Ψ^{LL}. The corresponding perturbation expansion of the Dirac equation, however, though feasible, suffers from the presence of strongly singular operators. It should be pointed out that in the DPT approach based on the Levy–Leblond equation both the Hamiltonian itself and the metric are involved, since both depend on the same parameter α. However, a formal separation of these two perturbations is possible and leads to some interesting results.

Let us for this purpose replace α on the right-hand side of Eqs. (1) and (2) by a formal parameter λ. Then Eq. (1) becomes

$$\begin{bmatrix} V & \boldsymbol{\sigma}\cdot\mathbf{p} \\ \boldsymbol{\sigma}\cdot\mathbf{p} & \alpha^2 V-2 \end{bmatrix}\Psi^D = W^D(S^0+\lambda^2 S^2)\Psi^D \quad (7)$$

and is accompanied by the normalization condition

$$\langle \Psi^D(\lambda)|S^0+\lambda^2 S^2|\Psi^D(\lambda)\rangle = \langle \varphi^D(\lambda)|\varphi^D(\lambda)\rangle + \lambda^2\langle \psi^D(\lambda)|\psi^D(\lambda)\rangle = 1, \quad (8)$$

where the λ dependence of the solutions is made explicit. Using Eqs. (7) and (8) as the basis of a λ^2-perturbation treatment,

$$W^D(\lambda) = W^0 + \lambda^2 W^2 + \lambda^4 W^4 + \cdots, \quad (9)$$

$$\Psi^D(\lambda) = \Psi^0 + \lambda^2\Psi^2 + \lambda^4\Psi^4 + \cdots, \quad (10)$$

and

$$\varphi^D(\lambda) = \varphi^0 + \lambda^2\varphi^2 + \lambda^4\varphi^4 + \cdots, \quad (11)$$

$$\psi^D(\lambda) = \psi^0 + \lambda^2\psi^2 + \lambda^4\psi^4 + \cdots, \quad (12)$$

one finds in zeroth order in λ^2

$$\begin{bmatrix} V & \boldsymbol{\sigma}\cdot\mathbf{p} \\ \boldsymbol{\sigma}\cdot\mathbf{p} & \alpha^2 V-2 \end{bmatrix}\begin{bmatrix} \varphi^0 \\ \psi^0 \end{bmatrix} = W^0 S^0 \begin{bmatrix} \varphi^0 \\ \psi^0 \end{bmatrix} = W^0 \begin{bmatrix} \varphi^0 \\ 0 \end{bmatrix}. \quad (13)$$

The elimination of the small component ψ^0 in the four-component Eq. (13), i.e.,

$$\psi^0 = \frac{1}{2-\alpha^2 V}\,\boldsymbol{\sigma}\cdot\mathbf{p}\varphi^0, \quad (14)$$

gives

$$\left[\boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{1}{2-\alpha^2 V}\,\boldsymbol{\sigma}\cdot\mathbf{p} + V\right]\varphi^0 = W^0\varphi^0, \quad (15)$$

with the normalization

$$\langle \Psi^0|S^0|\Psi^0\rangle = \langle \varphi^0|\varphi^0\rangle = 1. \quad (16)$$

We can immediately recognize Eqs. (15) and (16) as the regular approximation to the Dirac equation, proposed almost simultaneously by Heully *et al.*,[8] Durand,[9] and Chang, Pélissier, and Durand[10] and we shall refer to Eq. (15) by the acronym CPD. Several important features of this equation were studied in our earlier papers.[2–6] In particular a classical justification for Eq. (15) was given and it was shown to be an excellent approximation with several highly desirable mathematical properties, such as regularity and boundedness from below. This shows that the metric perturbation theory for Eq. (7) as given by expansions (11)–(14) corresponds to a regular perturbation treatment of the Dirac equation. The meaning of the zeroth-order approximation (15) and its validation can be achieved in terms of the inverse potential expansion that was used in Refs. 2 and 4. The four-component rather than two-component treatment of the perturbation expansion of Eq. (9) offers a direct way of deriving higher order CPD approximations which essentially amount to correcting Ψ^0

for normalization. Equation (13) which is neither nonrelativistic nor fully relativistic becomes a convenient zeroth-order approximation to Eq. (1).

In relation to DPT one can consider the present approach as a double perturbation expansion in terms of two formally independent parameters α^2 and λ^2. The zeroth-order Eq. (15) would then result from the infinite order summation of all α^2-dependent terms in the double perturbation version of DPT. Note that this infinite summation is responsible for removing all singular operators that otherwise arise in the case of attractive Coulomb singularities such as are present in atomic and molecular (Dirac–Fock) potentials.

III. HIGHER ORDER FOUR- AND TWO-COMPONENT REGULAR EQUATIONS

In first order with respect to λ^2 the renormalization perturbation theory for Eq. (7) gives

$$\begin{bmatrix} V-W^0 & \boldsymbol{\sigma}\cdot\mathbf{p} \\ \boldsymbol{\sigma}\cdot\mathbf{p} & \alpha^2 V-2 \end{bmatrix}\begin{bmatrix} \varphi^2 \\ \psi^2 \end{bmatrix}=(W^2S^0+W^0S^2)\begin{bmatrix} \varphi^0 \\ \psi^0 \end{bmatrix}, \tag{17}$$

where

$$W^2=-W^0\langle\psi^0|\psi^0\rangle$$
$$=-W^0\left\langle\varphi^0\left|\boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{1}{(2-\alpha^2V)^2}\,\boldsymbol{\sigma}\cdot\mathbf{p}\right|\varphi^0\right\rangle, \tag{18}$$

which can be seen to be identical to the result obtained in the FORA method of Refs. 2 and 3.

The calculation of higher order energies requires explicit knowledge of perturbed functions, which may be difficult to obtain for a general potential V. Rather than to consider order-by-order corrections resulting from the metric perturbation let us note that in terms of the metric perturbation theory the four-component treatment can be reduced to a two-component formalism at the level of the Dirac Eq. (7). For this purpose let us determine the small component $\psi^D(\lambda)$ from Eq. (7) as

$$\psi^D(\lambda)=\frac{1}{2-\alpha^2V-\lambda^2W^D(\lambda)}\,\boldsymbol{\sigma}\cdot\mathbf{p}\varphi^D(\lambda). \tag{19}$$

This leads to the following infinite order CPD-like equation for $\varphi^D(\lambda)$:

$$\left[\boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{1}{2-\alpha^2V-\lambda^2W^D(\lambda)}\,\boldsymbol{\sigma}\cdot\mathbf{p}+V\right]\varphi^D(\lambda)=W^D(\lambda)\varphi^D(\lambda). \tag{20}$$

The disturbing energy dependence of the effective Hamiltonian becomes immaterial in the perturbation treatment, since in a given order in λ^2 the effective operator is always determined by energies of lower order. Consequently the problems arising in the case of general energy-dependent and non-Hermitian effective Hamiltonians[10,19] disappear. In first order in λ^2 the effective operator on the left-hand side of Eq. (20) is found to be

$$\boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{1}{2-\alpha^2V}\,\boldsymbol{\sigma}\cdot\mathbf{p}+V-\lambda^2\boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{W^0}{(2-\alpha^2V)^2}\,\boldsymbol{\sigma}\cdot\mathbf{p}, \tag{21}$$

which can be recognized as the effective operator of the FORA method.[2,3]

In fact, as we shall see in the next sections, an excellent approximation to the Dirac wave function can be obtained by using Eqs. (19) and (20) directly, with the zeroth-order (CPD) energies in the denominator of the effective Hamiltonian. Such an approach gives an approximate wave function that is correct through at least first order in λ^2 and which we will refer to as the FCPD (first-order CPD) wave function

$$\left[\boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{1}{2-\alpha^2V-\alpha^2W^0}\,\boldsymbol{\sigma}\cdot\mathbf{p}+V\right]\varphi^{\mathrm{FCPD}}=W\varphi^{\mathrm{FCPD}} \tag{22}$$

and

$$\psi^{\mathrm{FCPD}}=\frac{1}{2-\alpha^2V-\alpha^2W^0}\,\boldsymbol{\sigma}\cdot\mathbf{p}\varphi^{\mathrm{FCPD}}. \tag{23}$$

IV. EXPECTATION VALUES

In order to assess the accuracy of the renormalization perturbation theory in comparison with the fully relativistic Dirac solutions, we now turn to the calculation of expectation values. For arbitrary values of λ^2, taking into account the changed metric,[1,12,13] one finds for the expectation value of an operator A

$$\langle A\rangle=\frac{\langle\Psi^D(\lambda)|(S^0+\lambda S^2)A(S^0+\lambda S^2)|\Psi^D(\lambda)\rangle}{\langle\Psi^D(\lambda)|S^0+\lambda^2S^2|\Psi^D(\lambda)\rangle}. \tag{24a}$$

For operators A which do not mix the large and small components of $\Psi^D(\lambda)$ Eq. (24a) simplifies to

$$\langle A\rangle=\frac{\langle\varphi^D(\lambda)|A|\varphi^D(\lambda)\rangle+\lambda^2\langle\psi^D(\lambda)|A|\psi^D(\lambda)\rangle}{\langle\varphi^D(\lambda)|\varphi^D(\lambda)\rangle+\lambda^2\langle\psi^D(\lambda)|\psi^D(\lambda)\rangle}. \tag{24b}$$

To zeroth order in λ^2 one simply recovers the CPD expression for expectation values

$$\langle A\rangle^{\mathrm{CPD}}=\langle\varphi^{\mathrm{CPD}}|A|\varphi^{\mathrm{CPD}}\rangle,\quad\langle\varphi^{\mathrm{CPD}}|\varphi^{\mathrm{CPD}}\rangle=1. \tag{25}$$

Although it is simple to write down the first-order corrections to the expectation values by expanding Eqs. (24) in powers of λ^2, it will turn out to be advantageous to proceed in slightly different way, namely by considering the four-component CPD wave function as an approximation to the Dirac wave function and simply calculating the expectation value according to Eqs. (24) with the four-component CPD wave function replacing the full Dirac solution

$$\langle A\rangle^{\mathrm{CPD\text{-}4}}=\frac{\langle\Psi^{\mathrm{CPD\text{-}4}}|(S^0+\alpha S^2)A(S^0+\alpha S^2)|\Psi^{\mathrm{CPD\text{-}4}}\rangle}{\langle\Psi^{\mathrm{CPD\text{-}4}}|S^0+\alpha^2S^2|\Psi^{\mathrm{CPD\text{-}4}}\rangle}$$
$$=\frac{\langle\varphi^{\mathrm{CPD}}|A|\varphi^{\mathrm{CPD}}\rangle+\alpha^2\langle\psi^{\mathrm{CPD}}|A|\psi^{\mathrm{CPD}}\rangle}{1+\alpha^2\langle\psi^{\mathrm{CPD}}|\psi^{\mathrm{CPD}}\rangle}, \tag{26}$$

where the small component CPD wave function is given by Eq. (14).

If we apply the first line of Eq. (26) to the case of the Dirac Hamiltonian H_D itself we obtain an improved equation for the energies

$$W^{\text{CPD-4}}=\frac{\langle\Psi^{\text{CPD-4}}|(S^0+\alpha S^2)H_D(S^0+\alpha S^2)|\Psi^{\text{CPD-4}}\rangle}{\langle\Psi^{\text{CPD-4}}|S^0+\alpha^2S^2|\Psi^{\text{CPD-4}}\rangle}$$

$$=\frac{\langle\Psi^{\text{CPD-4}}|H^D|\Psi^{\text{CPD-4}}\rangle}{\langle\Psi^{\text{CPD-4}}|S^0+\alpha^2S^2|\Psi^{\text{CPD-4}}\rangle}=\frac{W^{\text{CPD}}}{1+\alpha^2\langle\psi^{\text{CPD}}|\psi^{\text{CPD}}\rangle}$$

$$=\frac{W^{\text{CPD}}}{1+\alpha^2\langle\varphi^{\text{CPD}}|\boldsymbol{\sigma}\cdot\mathbf{p}\,\frac{1}{(2-\alpha^2V)^2}\,\boldsymbol{\sigma}\cdot\mathbf{p}|\varphi^{\text{CPD}}\rangle},\qquad(27)$$

where H^D is defined by Eq. (1)

This energy expression can be recognized as the ''scaled'' energy expression that was derived earlier by us using a different technique.[3,6] In fact it was shown that expression (27) gives the exact Dirac energy in the case of a hydrogenic potential and provides a very accurate approximation to the Dirac SCF-orbital energies even in an atom as heavy as uranium. These observations further justify the use of Eq. (26), rather than an expansion in powers of λ^2, for properties other than the energy as well. In the case of the energy the pure λ^2-order result is simply the FORA expression (18) which was earlier[2,3] shown to be considerably less accurate than Eq. (27).

Although Eq. (27) is only exact for a hydrogenic potential it is possible to derive an exact scaling relation between the Dirac and CPD energies that is valid for arbitrary potentials and all values of λ^2. Upon projecting Eq. (13) onto $\langle\Psi^D(\lambda)|$ one finds

$$W^D(\lambda)=W^{\text{CPD}}\,\frac{\langle\varphi^D(\lambda)|\varphi^{\text{CPD}}\rangle}{\langle\varphi^D(\lambda)|\varphi^{\text{CPD}}\rangle+\lambda^2\langle\psi^D(\lambda)|\psi^{\text{CPD}}\rangle},\qquad(28)$$

which reduces to Eq. (27) if one approximates the Dirac solution by its four-component CPD counterpart.

If one wants to further improve the expectation values, the four-component CPD wave function itself will have to be improved upon. This can be conveniently achieved by using the FCPD wave function of Eqs. (22) and (23) to obtain corrected energies as well as corrected expectation values, using Eq. (24) with this wave function. We will refer to these energies and expectation values as W^{FCPD} and $\langle A\rangle^{\text{FCPD}}$ (first-order CPD), respectively, since they are correct to first order in λ^2, although selected higher order contributions are present as well.

Actually once the CPD equation is solved, one can go even one step further. Then one has access to the improved energy $W^{\text{CPD-4}}$ of Eq. (27), which can subsequently be used in the denominators in Eqs. (22) and (23) instead of $W^0=W^{\text{CPD}}$ without incurring any additional computational effort. The resulting energies and expectation values will be referred to by the acronym FCPD-4.

We wish to point out that the two steps that are taken here, i.e., first adding a small component in the CPD-4 method and than improving the large component (which as we shall see is the main effect of the FCPD scheme) are indeed very similar to the effect of transforming the zeroth-order two-component CPD solution (which can be considered to be obtained in the Schrödinger picture)[2] back to the Dirac picture.[15,16] In present perturbation treatment, where picture changes never occur, such ''corrections'' to the wave function appear in higher order as they should.

TABLE I. Comparison of the radial expectation value $\langle r\rangle$ from the full Dirac densities and the CPD, CPD-4, FCPD, and FCPD-4 approximate densities (see the text) for the orbitals of the uranium atom in the DFT-LDA approximation. The errors Δ are given in percent $\Delta=(\langle r\rangle^{\text{Approx}}-\langle r\rangle^{\text{Dirac}})/\langle r\rangle^{\text{Dirac}}\times100\%$.

Orbital	$\langle r\rangle^{\text{Dirac}}$ (in a.u.)	Δ^{CPD}	$\Delta^{\text{CPD-4}}$	Δ^{FCPD}	$\Delta^{\text{FCPD-4}}$
$1s_{1/2}$	0.013 64	−11.555	−11.610	2.040	0.064
$2s_{1/2}$	0.056 50	−0.722	−2.239	0.131	0.058
$2p_{1/2}$	0.045 76	−0.291	−2.197	0.144	0.071
$2p_{3/2}$	0.055 99	−1.770	−1.814	0.089	0.039
$3s_{1/2}$	0.147 1	0.039	−0.598	0.052	0.045
$3p_{1/2}$	0.138 2	0.120	−0.575	0.056	0.049
$3p_{3/2}$	0.156 6	−0.114	−0.494	0.034	0.030
$3d_{3/2}$	0.135 0	−0.015	−0.462	0.025	0.021
$3d_{5/2}$	0.140 5	−0.407	−0.441	0.022	0.018
$4s_{1/2}$	0.319 9	0.093	−0.158	0.040	0.039
$4p_{1/2}$	0.318 2	0.115	−0.144	0.042	0.042
$4p_{3/2}$	0.354 9	0.048	−0.130	0.026	0.026
$4d_{3/2}$	0.351 5	0.068	−0.117	0.016	0.016
$4d_{5/2}$	0.362 5	−0.002	−0.112	0.014	0.014
$5s_{1/2}$	0.666 8	0.069	−0.017	0.037	0.037
$5p_{1/2}$	0.693 8	0.074	−0.009	0.039	0.039
$5p_{3/2}$	0.773 5	0.044	−0.016	0.022	0.022
$4f_{5/2}$	0.351 7	0.029	−0.084	0.005	0.004
$4f_{7/2}$	0.357 1	−0.058	−0.082	0.004	0.004
$5d_{3/2}$	0.867 3	0.035	−0.017	0.009	0.009
$5d_{5/2}$	0.895 8	0.021	−0.018	0.007	0.007
$6s_{1/2}$	1.473	0.049	0.026	0.038	0.038
$6p_{1/2}$	1.650	0.050	0.032	0.041	0.041
$6p_{3/2}$	1.897	0.026	0.013	0.020	0.020
$5f_{5/2}$	1.486	−0.042	−0.062	−0.059	−0.059
$5f_{7/2}$	1.547	−0.061	−0.074	−0.071	−0.071
$6d_{3/2}$	3.237	−0.015	−0.020	−0.018	−0.018
$6d_{5/2}$	3.497	−0.025	−0.029	−0.027	−0.027
$7s_{1/2}$	4.114	0.042	0.039	0.041	0.041

V. NUMERICAL RESULTS

In order to test the four methods (CPD, CPD-4, FCPD, and FCPD-4) described above, we have applied them to the case of the uranium atom in the framework of the density-functional local density approximation (DFT-LDA).[2,4,5] In all cases the density from the (normalized) large component only was used in the self-consistent determination of the Coulomb and exchange potentials. In order to assess the accuracy of the wave functions in distinct parts of space we calculated the orbital energies as well as the expectation values of several powers of the radial coordinate (r^2, r, r^{-1}, and r^{-2}) and compared them with the full Dirac values. The results of these calculations are presented in Tables I–V.

If we first concentrate on the valence (subvalence) orbitals we see from Tables I and II that for operators weighing the outer parts of the density (r^2,r) already the simple CPD method gives excellent results. The deviations from the full Dirac values never exceed 0.1% showing that the outer parts of the density are well represented in this approximation. In fact the more sophisticated methods hardly improve these results at all. However, if one considers the operators which weigh the inner tail of the density, i.e., r^{-1} and in particular

TABLE II. Comparison of the radial expectation value $\langle r^2\rangle$ from the full Dirac densities and the CPD, CPD-4, FCPD, and FCPD-4 approximate densities (see the text) for the orbitals of the uranium atom in the DFT-LDA approximation. The errors Δ are given in percent $\Delta=(\langle r^2\rangle^{\text{Approx}}-\langle r^2\rangle^{\text{Dirac}})/\langle r^2\rangle^{\text{Dirac}}\times 100\%$.

Orbital	$\langle r^2\rangle^{\text{Dirac}}$ (in a.u.)	Δ^{CPD}	$\Delta^{\text{CPD-4}}$	Δ^{FCPD}	$\Delta^{\text{FCPD-4}}$
$1s_{1/2}$	0.000 2615	−21.799	−21.891	4.122	0.126
$2s_{1/2}$	0.003 854	−2.805	−4.434	0.260	0.113
$2p_{1/2}$	0.002 656	−1.918	−4.365	0.279	0.134
$2p_{3/2}$	0.003 821	−3.531	−3.614	0.176	0.076
$3s_{1/2}$	0.024 94	−0.470	−1.193	0.103	0.090
$3p_{1/2}$	0.022 40	−0.299	−1.149	0.109	0.096
$3p_{3/2}$	0.028 53	−0.527	−0.988	0.068	0.059
$3d_{3/2}$	0.021 40	−0.275	−0.933	0.048	0.039
$3d_{5/2}$	0.023 03	−0.828	−0.891	0.042	0.034
$4s_{1/2}$	0.115 7	−0.028	−0.317	0.080	0.079
$4p_{1/2}$	0.115 4	0.021	−0.289	0.084	0.083
$4p_{3/2}$	0.143 1	−0.050	−0.259	0.053	0.052
$4d_{3/2}$	0.142 4	0.003	−0.235	0.032	0.031
$4d_{5/2}$	0.151 2	−0.086	−0.226	0.028	0.027
$5s_{1/2}$	0.497 3	0.063	−0.035	0.074	0.074
$5p_{1/2}$	0.540 7	0.079	−0.018	0.077	0.077
$5p_{3/2}$	0.671 7	0.036	−0.034	0.045	0.044
$4f_{5/2}$	0.144 9	−0.001	−0.174	0.009	0.008
$4f_{7/2}$	0.149 3	−0.124	−0.170	0.008	0.008
$5d_{3/2}$	0.854 8	0.028	−0.035	0.019	0.019
$5d_{5/2}$	0.911 7	0.009	−0.037	0.014	0.014
$6s_{1/2}$	2.423	0.077	0.052	0.076	0.076
$6p_{1/2}$	3.065	0.084	0.063	0.081	0.081
$6p_{3/2}$	4.061	0.040	0.026	0.039	0.039
$5f_{5/2}$	2.814	−0.131	−0.156	−0.148	−0.148
$5f_{7/2}$	3.094	−0.173	−0.190	−0.184	−0.184
$6d_{3/2}$	12.688	−0.040	−0.046	−0.042	−0.042
$6d_{5/2}$	14.936	−0.061	−0.065	−0.062	−0.062
$7s_{1/2}$	19.209	0.081	0.078	0.081	0.081

TABLE III. Comparison of the radial expectation value $\langle r^{-1}\rangle$ from the full Dirac densities and the CPD, CPD-4, FCPD, and FCPD-4 approximate densities (see the text) for the orbitals of the uranium atom in the DFT-LDA approximation. The errors Δ are given in percent $\Delta=(\langle r^{-1}\rangle^{\text{Approx}}-\langle r^{-1}\rangle^{\text{Dirac}})/\langle r^{-1}\rangle^{\text{Dirac}}\times 100\%$.

Orbital	$\langle r^{-1}\rangle^{\text{Dirac}}$ (in a.u.)	Δ^{CPD}	$\Delta^{\text{CPD-4}}$	Δ^{FCPD}	$\Delta^{\text{FCPD-4}}$
$1s_{1/2}$	122.998	13.024	13.105	−1.996	−0.065
$2s_{1/2}$	31.076	−4.805	2.316	−0.136	−0.062
$2p_{1/2}$	30.965	−4.669	2.219	−0.164	−0.092
$2p_{3/2}$	22.789	1.773	1.825	0.092	−0.043
$3s_{1/2}$	11.299	−5.140	0.626	−0.054	−0.047
$3p_{1/2}$	11.193	−4.960	0.576	−0.073	−0.066
$3p_{3/2}$	9.030	−0.625	0.498	−0.038	−0.033
$3d_{3/2}$	8.937	−0.536	0.452	−0.027	−0.023
$3d_{5/2}$	8.501	0.393	0.431	−0.023	−0.019
$4s_{1/2}$	4.843	−3.844	0.173	−0.041	−0.041
$4p_{1/2}$	4.730	−3.652	0.144	−0.054	−0.053
$4p_{3/2}$	3.983	−0.850	0.135	−0.028	−0.028
$4d_{3/2}$	3.805	−0.734	0.117	−0.018	−0.017
$4d_{5/2}$	3.651	−0.194	0.113	−0.015	−0.015
$5s_{1/2}$	2.151	−2.418	0.019	−0.039	−0.039
$5p_{1/2}$	2.038	−2.223	0.004	−0.047	−0.047
$5p_{3/2}$	1.760	−0.607	0.018	−0.023	−0.023
$4f_{5/2}$	3.386	−0.140	0.078	−0.005	−0.005
$4f_{7/2}$	3.328	0.048	0.076	−0.005	−0.005
$5d_{3/2}$	1.537	−0.475	0.017	−0.010	−0.010
$5d_{5/2}$	1.479	−0.207	0.019	−0.007	−0.007
$6s_{1/2}$	0.9059	−1.225	−0.028	−0.040	−0.040
$6p_{1/2}$	0.7997	−1.032	−0.036	−0.046	−0.046
$6p_{3/2}$	0.6814	−0.288	−0.014	−0.021	−0.021
$5f_{5/2}$	0.9181	−0.069	0.045	0.042	0.042
$5f_{7/2}$	0.8885	−0.005	0.051	0.049	0.049
$6d_{3/2}$	0.4054	−0.111	0.016	0.015	0.015
$6d_{5/2}$	0.3762	−0.036	0.024	0.023	0.023
$7s_{1/2}$	0.3059	−0.409	−0.041	−0.042	−0.042

r^{-2}, it is seen from Tables III and IV that the accuracy of the CPD density is considerably lower in this region, giving errors of up to almost 40% for the subvalence $6p_{1/2}$ and 14% for the valence $7s_{1/2}$ orbital in the r^{-2} expectation value. In Figs. 1 and 2 we show the inner part of the densities of $7s_{1/2}$ and the $6p_{1/2}$ orbital, respectively. It is clear from Figs. 1 and 2 that the lack of a small component in the CPD density is largely responsible for the inaccuracies in the inner region. In particular, due to the fact that the small and large Dirac components do not vanish at the same radial distances, the CPD densities exhibit nodes that are absent in the Dirac densities. Introduction of a small component through the CPD-4 scheme completely remedies the defects of the CPD method and the corresponding expectation values from Tables III and IV are again very accurate indeed. The deviations of the CPD-4 (as well as the FCPD and FCPD-4) densities from the Dirac densities are in fact invisible on the scale of Figs. 1 and 2. The FCPD and FCPD-4 methods, that mostly modify the form of the large component, hardly improve the already very accurate CPD-4 densities for the valence orbitals, showing that the form of the CPD large component is in fact of quite high quality. Obviously in the region close to the nucleus the small component becomes essential, but in the case of valence (subvalence) orbitals its form is well represented by Eq. (14) relating it to the large component.

In Table V we also present the orbital energies, which are seen to be excellent already at the CPD level for the valence (subvalence) levels and again they are hardly improved upon at all by the more elaborate schemes. This shows that the orbital energies are less sensitive to the core tails of the orbitals than their constituent parts, since the potential contribution (and therefore the kinetic contribution as well) can be expected to have a similar accuracy as the r^{-1} expectation values discussed above.

Turning now to the (deep) core orbitals the picture changes considerably. First of all the CPD expectation values are rather inaccurate even for the operators weighing the outer tail (r^2,r) with errors of up to more than 20% for the r^2 expectation value of the $1s_{1/2}$ orbital. As Tables I–IV clearly show, now, in contrast to the situation for the valence (subvalence) orbitals, this failure is not remedied at all by adding a small component in the CPD-4 fashion. In fact in the case of the $1s_{1/2}$ the expectation values hardly change at all when passing from CPD to CPD-4. This, at first sight unexpected, behavior can be understood by considering the form of the hydrogenic Dirac wave functions. For these functions the small and large component radial densities are proportional to each other for solutions corresponding to the lowest principal quantum number for each total angular momentum j (i.e., $1s_{1/2}$, $2p_{3/2}$, $3d_{5/2}$, $4f_{7/2}$, etc.). Since the

TABLE IV. Comparison of the radial expectation value $\langle r^{-2}\rangle$ from the full Dirac densities and the CPD, CPD-4, FCPD, and FCPD-4 approximate densities (see the text) for the orbitals of the uranium atom in the DFT-LDA approximation. The errors Δ are given in percent $\Delta=(\langle r^{-2}\rangle^{\text{Approx}}-\langle r^{-2}\rangle^{\text{Dirac}})/\langle r^{-2}\rangle^{\text{Dirac}}\times 100\%$.

Orbital	$\langle r^{-2}\rangle^{\text{Dirac}}$ (in a.u.)	Δ^{CPD}	$\Delta^{\text{CPD-4}}$	Δ^{FCPD}	$\Delta^{\text{FCPD-4}}$
$1s_{1/2}$	45785.118	27.556	27.747	−3.926	−0.127
$2s_{1/2}$	7345.948	−7.747	4.610	−0.273	−0.127
$2p_{1/2}$	2178.797	−34.147	4.433	−0.391	−0.246
$2p_{3/2}$	713.500	3.541	3.656	−0.190	−0.093
$3s_{1/2}$	1737.441	−12.711	1.213	−0.121	−0.107
$3p_{1/2}$	535.413	−39.512	1.056	−0.238	−0.225
$3p_{3/2}$	177.278	−1.470	0.965	−0.089	−0.080
$3d_{3/2}$	100.694	−2.485	0.892	−0.058	−0.050
$3d_{5/2}$	89.012	0.769	0.850	−0.048	−0.041
$4s_{1/2}$	475.374	−14.036	0.320	−0.101	−0.100
$4p_{1/2}$	145.033	−40.308	0.177	−0.217	−0.216
$4p_{3/2}$	48.503	−2.770	0.246	−0.074	−0.073
$4d_{3/2}$	26.382	−3.784	0.219	−0.043	−0.042
$4d_{5/2}$	23.333	−0.535	0.213	−0.034	−0.033
$5s_{1/2}$	122.800	−14.431	0.017	−0.101	−0.101
$5p_{1/2}$	35.733	−39.849	−0.112	−0.214	−0.214
$5p_{3/2}$	12.142	−3.064	0.016	−0.065	−0.065
$4f_{5/2}$	13.923	−0.505	0.149	−0.012	−0.011
$4f_{7/2}$	13.404	0.085	0.145	−0.010	−0.010
$5d_{3/2}$	5.737	−3.795	0.024	−0.028	−0.028
$5d_{5/2}$	5.067	−0.839	0.031	−0.018	−0.018
$6s_{1/2}$	24.922	−14.456	−0.082	−0.109	−0.109
$6p_{1/2}$	6.305	−38.603	−0.201	−0.221	−0.221
$6p_{3/2}$	2.063	−2.933	−0.048	−0.062	−0.062
$5f_{5/2}$	1.516	−0.564	0.077	0.072	0.072
$5f_{7/2}$	1.419	−0.115	0.086	0.083	0.083
$6d_{3/2}$	0.4560	−2.968	0.026	0.023	0.023
$6d_{5/2}$	0.3739	−0.652	0.047	0.044	0.044
$7s_{1/2}$	2.596	−14.236	−0.116	−0.120	−0.120

TABLE V. Comparison of the orbital energies ϵ from the full Dirac equation and the CPD, CPD-4, FCPD, and FCPD-4 approximations (see the text) for the uranium atom in the DFT-LDA approximation. The errors Δ are given in percent $\Delta=(\epsilon^{\text{Approx}}-\epsilon^{\text{Dirac}})/\epsilon^{\text{Dirac}}\times 100\%$.

Orbital	ϵ^{Dirac} (in a.u.)	Δ^{CPD}	$\Delta^{\text{CPD-4}}$	Δ^{FCPD}	$\Delta^{\text{FCPD-4}}$
$1s_{1/2}$	−4255.56	14.509	−0.127	−2.242	−0.105
$2s_{1/2}$	−795.009	3.013	−0.091	−0.183	−0.086
$2p_{1/2}$	−766.703	3.022	−0.093	−0.185	−0.088
$2p_{3/2}$	−625.961	2.562	−0.061	−0.125	−0.057
$3s_{1/2}$	−200.691	0.968	−0.075	−0.085	−0.074
$3p_{1/2}$	−187.820	0.962	−0.077	−0.086	−0.076
$3p_{3/2}$	−155.385	0.850	−0.048	−0.055	−0.048
$3d_{3/2}$	−134.987	0.859	−0.029	−0.036	−0.028
$3d_{5/2}$	−128.402	0.829	−0.025	−0.031	−0.023
$4s_{1/2}$	−51.0914	0.302	−0.074	−0.075	−0.074
$4p_{1/2}$	−45.2956	0.289	−0.077	−0.078	−0.076
$4p_{3/2}$	−36.8264	0.265	−0.047	−0.048	−0.047
$4d_{3/2}$	−27.5899	0.266	−0.025	−0.026	−0.025
$4d_{5/2}$	−26.0319	0.257	−0.021	−0.022	−0.021
$5s_{1/2}$	−11.3270	0.049	−0.072	−0.072	−0.072
$5p_{1/2}$	−9.0734	0.037	−0.075	−0.075	−0.075
$5p_{3/2}$	−7.0577	0.055	−0.038	−0.038	−0.038
$4f_{5/2}$	−13.8786	0.249	0.004	0.004	0.004
$4f_{7/2}$	−13.4722	0.244	0.006	0.005	0.006
$5d_{3/2}$	−3.7644	0.070	−0.003	−0.003	−0.003
$5d_{5/2}$	−3.4659	0.072	0.003	0.003	0.003
$6s_{1/2}$	−1.7198	−0.049	−0.078	−0.078	−0.078
$6p_{1/2}$	−1.0694	−0.062	−0.085	−0.085	−0.085
$6p_{3/2}$	−0.7410	−0.013	−0.031	−0.031	−0.031
$5f_{5/2}$	−0.1033	0.707	0.678	0.668	0.668
$5f_{7/2}$	−0.0728	0.961	0.934	0.934	0.934
$6d_{3/2}$	−0.0710	0.141	0.141	0.141	0.141
$6d_{5/2}$	−0.0537	0.186	0.168	0.168	0.168
$7s_{1/2}$	−0.134	−0.075	−0.075	−0.075	−0.075

field in which the $1s_{1/2}$ electrons move is largely hydrogenic in nature, the transfer of density from the large to the small component as is done in the CPD-4 method, hardly affects the total density at all. The same is seen to be true to a somewhat lesser extent for the $2p_{3/2}$ and $3d_{5/2}$ orbitals, although there of course deviations from purely hydrogenic behavior become more prominent. The main problem in the deep core region is that the large CPD component itself is not accurate enough and in fact is too contracted compared to the Dirac large component. This is to be expected if one recalls[3] the (contractive) scaling relation between the CPD (large component) wave function and the Dirac large component in the hydrogenic case. This contraction leads to too small expectation values of r^2 and r in Tables I and II and to too large values for r^{-1} and r^{-2} in Tables III and IV. This contraction can be clearly seen in Fig. 3 for the $1s_{1/2}$ orbital in both the CPD and (almost equal, *vide supra*) CPD-4 densities. In orbitals other than $1s_{1/2}$, $2p_{3/2}$, $3d_{5/2}$ the small and large component radial densities are no longer proportional even in a hydrogenic potential and the absence of a small component contribution partly compensates for the too contracted *large* component density, leading to perhaps fortuitously accurate values for $\langle r\rangle$. Introducing a small component density in the CPD-4 method then leads to less accurate results since the cancelation no longer takes place, while the large component is still too contracted. On the other hand if one looks at the r^{-2} expectation value for e.g., the $2p_{1/2}$ in Table IV, it is clear that the absence of a small component in the CPD wave function leads to insufficiently contracted *total* densities, as is also evident from Fig. 4. This effect is particularly strong for $p_{1/2}$ orbitals, since these have compact small components of a $s_{1/2}$-like form and indeed the $p_{1/2}$ expectation values are improved considerably by the introduction of a small component in CPD-4.

In order to improve the large component one has to go to the FCPD or FCPD-4 scheme and indeed Tables I–IV show that already the FCPD method is capable of providing very accurate expectation values for all operators considered. Only in the case of the $1s_{1/2}$ orbital do we see an appreciable improvement of FCPD-4 over FCPD. In Fig. 3 for the $1s_{1/2}$ density we see that the Dirac density is very well reproduced by both the FCPD and FCPD-4 densities, only the former showing a small but distinguishable deviation on this scale near the maximum of the density.

As shown in Table V the energies of the core orbitals are, in contrast to the valence orbital energies, not represented very accurately at the CPD level, with errors up to almost 15% for the $1s_{1/2}$ orbital. However, the CPD-4 energies (i.e., the ''scaled'' energies discussed before in Ref. 3) are seen to be very accurate indeed, which at first sight seems a little surprising in the light of the earlier discussion of the

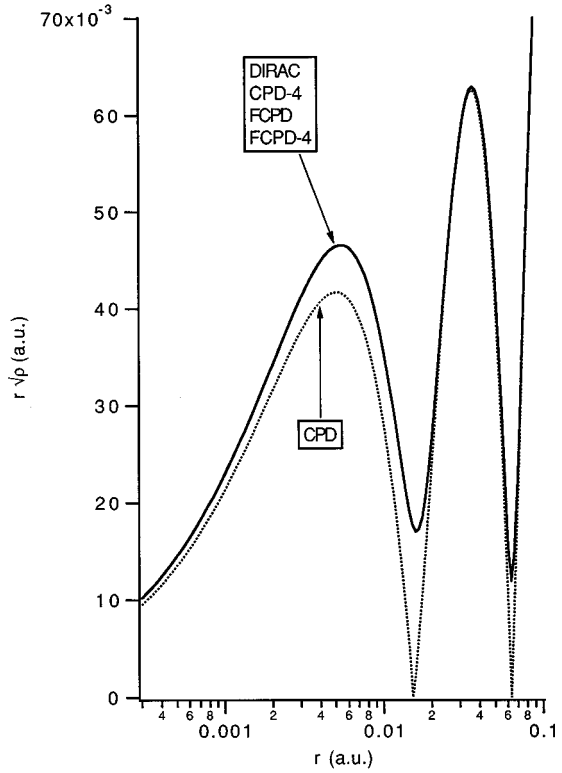

FIG. 1. Comparison of the inner part of the full Dirac $7s_{1/2}$ density with the approximate (CPD, CPD-4, FCPD, and FCPD-4, see the text) densities for the uranium atom.

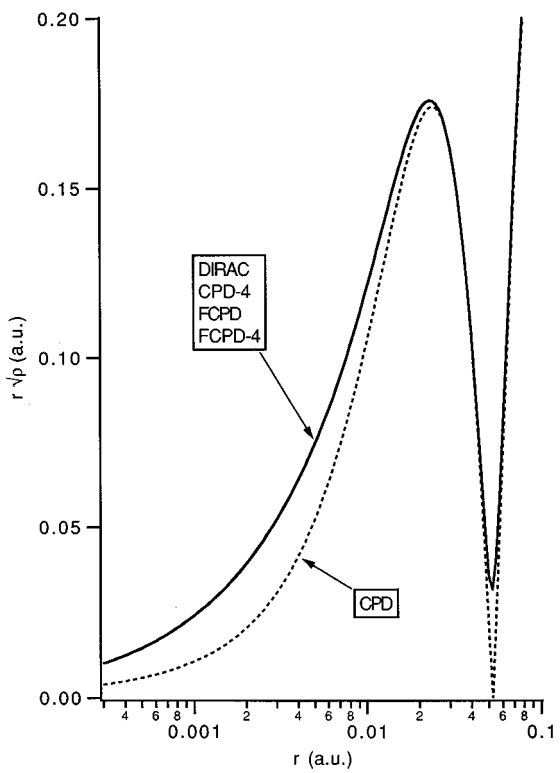

FIG. 2. Comparison of the inner part of the full Dirac $6p_{1/2}$ density with the approximate (CPD, CPD-4, FCPD, and FCPD-4, see the text) densities for the uranium atom.

other expectation values, where the CPD-4 method hardly improved upon the CPD results for the core orbitals. The explanation of the accuracy of the CPD-4 energies lies in the fact,[3] mentioned in Sec. IV, that the CPD-4 energy expression Eq. (27) actually gives the *exact* Dirac energies in the case of a hydrogenic potential. Although the self-consistent field experienced by the core electrons is of course not exactly hydrogenic, this property of the CPD-4 energy expression can still be held responsible for its accuracy in the core region. Note, however, that this does not imply that the CPD-4 wave functions themselves are very accurate in the core region. In fact they are not, as was evident from the expectation value results. It merely shows that in the case of hydrogen the exact Dirac wave function and the CPD-4 wave function have identical energy expectation values. Actually this equality even holds for the hydrogenic $1s_{1/2}$ ground state and would contradict the variational principle if the Dirac equation did not possess a negative energy spectrum unbounded from below.

The accuracy of the CPD-4 energies across the whole range examined in Table V should therefore be ascribed to two different sources depending on the part of the spectrum considered; in the core the wave functions themselves are not very accurate, but the energies remain quite good due to the exactness of CPD-4 for hydrogen, while in the valence region the CPD-4 wave functions themselves are quite close to the full Dirac solution, so that their energies are accurate as well.

It is also apparent from Table V that the FCPD method performs somewhat worse for the energies than CPD-4, even though, as we have seen, the wave functions and densities are considerably improved judging from the expectation values in Tables I–IV. This can be understood from the fact that although the wave functions are better, the hydrogenic exactness property of the energy expression (27) is lost at this level. If we finally go to the FCPD-4 approximation, the wave functions are so close to the full Dirac solutions that the energies become very accurate as well, with remaining errors at about the same level as for the CPD-4 energies.

Finally it should be pointed out that, as mentioned before, in all calculations presented here, the self-consistent potential was determined from the (normalized) large component alone, rather than from the full density corresponding to the wave functions under consideration. This of course introduces additional deviations from the fully self-consistent Dirac solutions. However, as the FCPD-4 results in Tables I–V show, the corresponding errors are very small for both the energies and the expectation values. The largest deviations are found in the $5f$ shell, as is seen especially in Tables II and V. This is to be expected since the $5f$ orbitals are the most sensitive to the indirect effects of the self-consistent potential as was analyzed in detail earlier by Schwarz *et al.*[20] It should therefore be quite feasible to perform reasonably accurate *ab initio* Dirac–Fock calculations using the density from the large Dirac component alone, *provided* it is renormalized to the correct number of electrons.

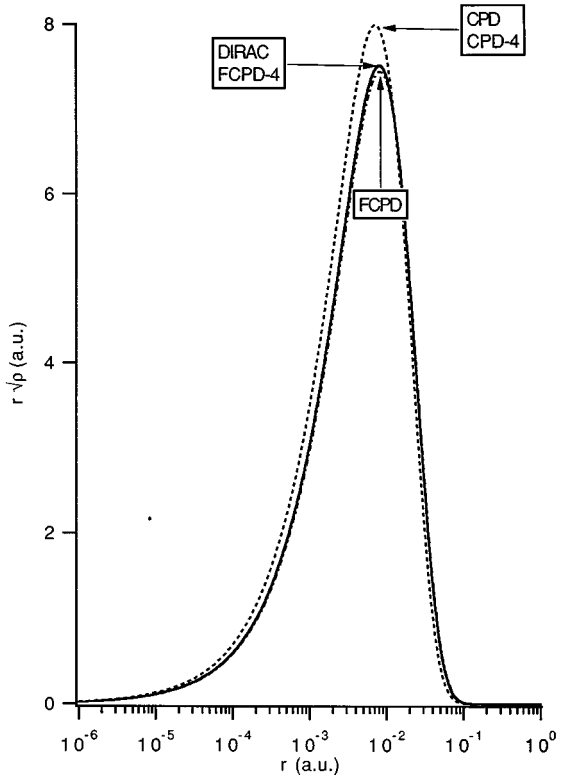

FIG. 3. Comparison of the full Dirac $1s_{1/2}$ density with the approximate (CPD, CPD-4, FCPD, and FCPD-4, see the text) densities for the uranium atom.

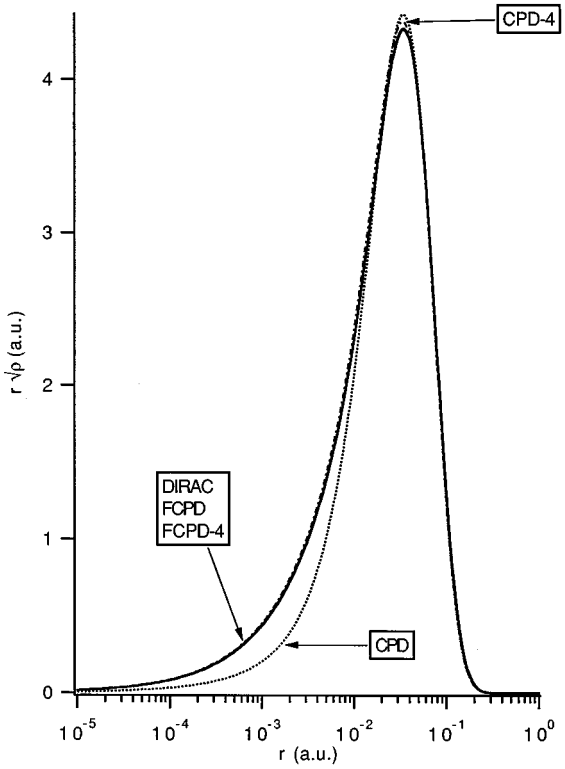

FIG. 4. Comparison of the full Dirac $2p_{1/2}$ density with the approximate (CPD, CPD-4, FCPD, and FCPD-4, see the text) densities for the uranium atom.

This obviates the need to calculate a large number of the two-electron integrals that involve the small component basis. Such a scheme would, without sacrificing much in accuracy, be considerably more efficient than implementations that calculate all integrals.

VI. CONCLUSIONS

By combining the ideas of the regular Hamiltonian method for solving Dirac's equation with the direct perturbation technique of Rutkowski and Kutzelnigg, the relativistic one-electron equation for arbitrary potentials has been cast into a form suitable for nonsingular perturbation theory. This was achieved by considering the relativistic change in the Hamiltonian and the change in the metric which both enter the DPT approach as independent perturbations. The perturbation series for the Hamiltonian can then be summed to infinite order and one is left with the metric perturbation alone, while at the same time all singularities in the operators have disappeared.

At the lowest level of approximation in the metric perturbation one recovers the CPD method that was extensively studied before. However, the current formulation suggests a four-component extension (called CPD-4) that provides us with substantially improved densities by introducing a small component which can be calculated without appreciable additional effort. The CPD-4 energies were shown to be identical to the scaled energies considered in our earlier publications, and are very accurate across the whole energy scale from the deep core all the way up to the valence levels.

We have also studied the expectation values for various powers of the radial coordinate r. It was shown that for the valence (subvalence) orbitals the simple CPD method gives accurate results for operators weighing the outer regions of the atom, but fails for negative powers of r that emphasize the inner parts of the density. However, in these last cases the CPD-4 method almost completely corrects the CPD errors, showing that they are mainly due to the lack of a small component.

For the core levels the situation is rather different. It was shown that here the errors mainly arise from an inaccurate form of the large component, which cannot be corrected for by merely introducing a small component as in the CPD-4 method. Hence it becomes essential to extend the renormalization perturbation theory to higher orders. The lowest order extension results in two improvements over the CPD and CPD-4 approximations (FCPD and FCPD-4) that were shown to indeed correct the deficiencies in the large component. The resulting expectation values then become very good even for the core levels.

The fact that the CPD-4 energies, unlike other expectation values, are also highly accurate even in the core region should be attributed to the fact that the corresponding energy expression gives the exact Dirac energies in the case of hydrogenic potentials, even though the CPD-4 wave functions may not be very accurate in this energy range.

Finally in all calculations the self-consistent potential

was determined from the renormalized large component density alone. The fact that the FCPD (FCPD-4) results (both energies and expectation values) are nevertheless very accurate suggests that also in traditional *ab initio* methods it should be a good approximation to use only the large component of the density in the SCF potential, provided it is renormalized to the correct number of electrons.

ACKNOWLEDGMENT

The authors gratefully acknowledge a research grant from the European Science Foundation through its Relativistic Effects in Heavy Elements programme.

[1] W. Kutzelnigg, Z. Phys. D **15**, 27 (1990).
[2] E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **99**, 4597 (1993).
[3] R. van Leeuwen, E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **101**, 1272 (1994).
[4] E. van Lenthe, R. van Leeuwen, E. J. Baerends, and J. G. Snijders, in *New Challenges in Computational Quantum Chemistry*, Proceedings of the Symposion in honour of W. C. Nieuwpoort, edited by R. Broer, P. J. C. Aerts, and P. S. Bagus (Groningen U. P., Groningen, 1994), pp. 93–111.
[5] E. van Lenthe, R. van Leeuwen, E. J. Baerends, and J. G. Snijders, Int. J. Quantum Chem. (to be published).
[6] E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **101**, 9783 (1994).
[7] A. J. Sadlej and J. G. Snijders, Chem. Phys. Lett. **229**, 435 (1994).
[8] J.-L. Heully, I. Lindgren, E. Lindroth, S. Lundqvist, and A-M. Mårtensson-Pendrill, J. Phys. B **19**, 2799 (1986).
[9] P. Durand, C. R. Acad. Sci. Paris **2**, 119 (1986).
[10] Ch. Chang, M. Pélissier, and P. Durand, Phys. Scr. **34**, 394 (1986).
[11] A. Rutkowski, J. Phys. B **19**, 149 (1986).
[12] W. Kutzelnigg, Z. Phys. D **11**, 15 (1989).
[13] W. Kutzelnigg, R. Franke, E. Ottschofski, and W. Klopper, in Ref. 4, pp. 112–133.
[14] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).
[15] J. G. Snijders and P. Pyykkö, Chem. Phys. Lett. **75**, 5 (1980).
[16] E. J. Baerends, W. H. E. Schwarz, P. Schwerdtfeger, and J. G. Snijders, J. Phys. B **23**, 3225 (1990).
[17] J. M. Levy-Leblond, Comm. Math, Phys. **6**, 286 (1967).
[18] J. M. Levy-Leblond, Ann. Phys. (NY) **57**, 481 (1970).
[19] P. Durand and J-P. Malrieu, Adv. Chem. Phys. **67**, 321 (1987).
[20] W. H. E. Schwarz, E. M. van Wezenbeek, E. J. Baerends, and J. G. Snijders, J. Phys. B **22**, 1515 (1989).